

Asymptotics for the survival probability of a Rouse chain monomer

G. OSHANIN^(a)

Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie (Paris 6) - 4 Place Jussieu, 75252 Paris, France

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Abstract. - We study the long-time asymptotical behavior of the survival probability P_t of a tagged monomer of an infinitely long Rouse chain in presence of two fixed absorbing boundaries, placed at $x = \pm L$. Mean-square displacement of a tagged monomer obeys $\overline{X^2(t)} \sim t^{1/2}$ at all times, which signifies that its dynamics is an anomalous diffusion process. Constructing lower and upper bounds on P_t , which have the same time-dependence but slightly differ by numerical factors in the definition of the characteristic relaxation time, we show that P_t is a stretched-exponential function of time, $\ln(P_t) \sim -t^{1/2}/L^2$. This implies that the distribution function of the first exit time from a fixed interval $[-L, L]$ for such an anomalous diffusion has all moments.

Introduction. - Dynamics of a tagged monomer (TM) of a polymer chain in solution is a practically important physical example of an anomalous diffusive process. While dynamics of the whole chain is dominated by the motion of its center of mass which moves diffusively, dynamics of a TM is coupled to dynamics of other monomers; as time evolves, progressively more and more other monomers start to impede dynamics of the TM, which ultimately results in a subdiffusive motion. Such subdiffusive motion persists up to a certain characteristic time, proportional to some power of the chain length; at greater times conventional diffusive behavior is established [1].

For the so-called Rouse model of a polymer chain [2], in which a chain is considered as a series of K beads linearly connected by harmonic springs, the TM mean-square displacement $\overline{X^2(t)}$ can be calculated exactly. One finds an anomalous diffusion law $\overline{X^2(t)} \sim \sqrt{t}$ for times less than the so-called Rouse relaxation time $T_R \sim K^2$, (the time needed for some perturbation, i.e. a kink, to spread diffusively along the whole chain), and conventional diffusive motion with reduced, by factor K , diffusion coefficient for times larger than T_R . In fact, for the Rouse model many important dynamical properties can be calculated exactly, e.g., the TM position probability distribution function, the dynamical structure factor [1], as well as the measure of different trajectories of a tagged monomer [3]. One may even determine exactly the dynamics of the TM of a Rouse

chain in more complex situations - in random layered flows [4, 5] or in situations appropriate to electrophoresis of polyampholytes, i.e., polymers whose monomers may be positively or negatively charged and the chain is subject to external electric field [6].

Recently, following a general interest in understanding subdiffusive and superdiffusive motion, a different aspect of anomalous diffusion of tagged monomers of a Rouse polymer chain has attracted some attention. Namely, dynamics of a Rouse chain in presence of traps or absorbing boundaries reacting with some or just one of its monomers has been analysed [7–9]. Physically, such a situation is realized for polymers diffusing on solid surfaces containing chemically active sites, which may react reversibly or irreversibly with any or some of the chain monomers temporarily or completely anchoring the chain. Conceptually, this question is interesting in its own right since the answer contains a solution, for anomalous diffusion, of a certain first-passage time problem, whose general understanding is a basic aspect of stochastic processes [10].

Dynamics of a TM of an infinitely long Rouse chain in one-dimensional systems in presence of two absorbing boundaries has been analysed in Ref. [8] within a path-integral formalism with an exact measure of trajectories of such a monomer [3], and a suitably extended classic method of images. It was shown that the probability P_t that the tagged monomer commencing its motion at the origin does not escape, during time t , from the interval $[-L, L]$, or, in other words, that it "survives" up to time

^(a) E-mail: oshanin@lptl.jussieu.fr

t in presence of two traps placed at $x = -L$ and $x = L$, obeys

$$\ln(P_t) \sim -\frac{t^{1/2}}{L^2}, \quad (1)$$

i.e., the decay of P_t is described by a stretched-exponential function of time. The law in Eq.(1) has been previously conjectured using heuristic arguments in Ref. [7].

On the other hand, dynamics of a tagged monomer of a finite Rouse chain in one-dimension in presence of absorbing boundaries has been analysed numerically in Ref. [9]. Here it was claimed that P_t is an exponential function of time

$$\ln(P_t) \sim -t, \quad (2)$$

and thus decays at a faster rate. Consequently, the results of Refs. [7,8] and [9] are in an apparent contradiction with each other.

In this Letter we aim to resolve this controversy by deriving, using the approach outlined in Ref. [11], rigorous lower and upper bounds on the survival probability P_t of a Rouse chain monomer in a one-dimensional system with two absorbing boundaries. We set out to show here that P_t obeys the following double-sided inequality

$$\frac{1}{4} \leq \frac{-\ln(P_t)}{t^{1/2}} \left(\frac{4L^2}{\pi^{3/2}} \right) \leq 1, \quad (3)$$

which defines the decay law up to a numerical factor in the characteristic relaxation time. This inequality confirms the result in Eq.(1) and rules out the result in Eq.(2).

This paper is outlined as follows: In section 2 we present the notations and write down basic equations. In section 3 we present the results of a heuristic approach, in which the survival probability of a tagged Rouse chain monomer in presence of two absorbing boundaries at $x = \pm L$ is interpreted as the survival probability of a Brownian motion in presence of absorbing boundaries which move away from the origin as $\pm Lt^{1/4}$. Next, in section 4 we derive rigorous lower and upper bounds on P_t , which lead to the inequality in Eq.(3). Finally, in section 5, we conclude with a brief recapitulation of our results and discussion.

Notations and basic equations. – Dynamics of a discrete Rouse chain comprising an infinite number of monomers is described by a set of Langevin equations [1]:

$$\frac{dX_n(t)}{dt} = \frac{1}{2} (X_{n+1}(t) + X_{n-1}(t) - 2X_n(t)) + \zeta_t^{(n)}, \quad (4)$$

$X_n(t)$ being an instantaneous position of the n -th bead, $-\infty < n < \infty$, and $\zeta_t^{(n)}$ - independent Gaussian white-noise processes, such that

$$\overline{\zeta_t^{(n)}} = 0, \quad \overline{\zeta_t^{(n)} \zeta_{t'}^{(m)}} = \delta_{n,m} \delta(t - t'). \quad (5)$$

In Eq.(5), the bar denotes averaging over thermal histories, $\delta_{n,m}$ is the Kronecker symbol and $\delta(t)$ is the delta-function. Note that, for simplicity of presentation, we have set in Eq.(4) the friction constant equal to 1, the

spring constant and the temperature equal to 1/2. These parameters can be easily restored in our final results.

Note, as well, that Eq.(4) describes the time evolution of local heights of the Edwards-Wilkinson interface [12] in one dimension, or the time evolution of the difference of local concentrations of A and B species for diffusion-limited $A + B \rightarrow \text{inert}$ reactions with random, steady, uncorrelated input of A and B [13]. Our results will thus apply to these systems too.

Supposing that initially all monomers are at the origin, we have that $X_{n=0}(t)$ - position of the zeroth TM of an infinitely long Rouse chain at time t - for a given realization of noises $\zeta_t^{(n)}$ is determined as a portfolio of independent Gaussian processes:

$$X_{n=0}(t) \equiv X(t) = \sum_{n=-\infty}^{\infty} \int_0^t d\tau \zeta_\tau^{(n)} e^{-(t-\tau)} I_n(t-\tau), \quad (6)$$

where $I_n(t-\tau)$ is the modified Bessel function of order n . Eq.(6) yields the following expression for the mean-square displacement of the zeroth monomer of an infinitely long Rouse chain:

$$\overline{X^2(t)} = te^{-2t} [I_0(2t) + I_1(2t)] = \sqrt{\frac{t}{\pi}} + o(\sqrt{t}). \quad (7)$$

As a matter of fact, any other initial condition can be considered. However, the effect of the initial state of the chain on the process in Eq.(6) fades out quite rapidly; it was observed in Ref. [9] that the difference in dynamics between the case when initially all monomers are at the origin or when one starts from an equilibrated configuration is rather small. Thus we have chosen the simplest case when $X_n(t=0) = 0$ for any n .

We note next that since we are concerned with the large- t behavior, it will not matter much how we define $\zeta_t^{(n)}$ - as continuous in time functions or as discrete processes, provided that we keep all essential features of noise. We thus divide, at fixed t , the interval $[0, t]$ into N ($N \gg 1$) small subintervals Δ , (such that $\Delta N \equiv t$), and assume that $\zeta_t^{(n)}$ is constant and equal to $\zeta_k^{(n)}/\sqrt{\Delta}$ within the k -th subinterval, $k = 0, 1, \dots, N-1$. We suppose that $\{\zeta_k^{(n)}\}$ is an infinite set of independent random variables with normal distribution $N[0, 1]$.

Then, $X(t)$ can be written down as a weighted sum of an infinite number of independent discrete noise processes:

$$X(t) = \sum_{n=-\infty}^{\infty} \sum_{l=1}^N \sigma_l^{(n)} \zeta_{N-l}^{(n)}, \quad (8)$$

with l and n -dependent weights

$$\sigma_l^{(n)} = \frac{1}{\sqrt{\Delta}} \int_{\Delta(l-1)}^{\Delta l} du e^{-u} I_n(u). \quad (9)$$

At this point, it is also expedient to introduce another property - an effective time-dependent variance $\tilde{\sigma}_l^2$ - which

will emerge in what follows as the key parameter. Squaring Eq.(8) and averaging the resulting expression with respect to distributions of i.i.d. variables $\{\zeta_k^{(n)}\}$, we get

$$\overline{X^2(t)} = \sum_{l=1}^N \tilde{\sigma}_l^2, \quad (10)$$

where the effective variance $\tilde{\sigma}_l^2$ is given by

$$\begin{aligned} \tilde{\sigma}_l^2 &= \sum_{n=-\infty}^{\infty} \left(\sigma_l^{(n)} \right)^2 = \\ &= \frac{1}{\Delta} \int_{\Delta(l-1)}^{\Delta l} du_1 \int_{\Delta(l-1)}^{\Delta l} du_2 e^{-u_1 - u_2} I_0(u_1 + u_2). \end{aligned} \quad (11)$$

The integrations in Eq.(11) can be performed exactly, but the resulting expression - a combination on nine modified Bessel functions - is rather cumbersome and is of a little use. In fact, all information we need to know about $\tilde{\sigma}_l^2$ can be extracted directly from Eq.(11):

(a) $\tilde{\sigma}_l^2$ is a *monotonically decreasing* function of l . To see this, it suffice to notice that $\exp(-x)I_0(x)$ is a monotonically decreasing function of x ; then, one finds from Eq.(11) that $\tilde{\sigma}_l^2$ obeys the following double-sided inequality:

$$\Delta e^{-2\Delta l} I_0(2\Delta l) \leq \tilde{\sigma}_l^2 \leq \Delta e^{-2\Delta(l-1)} I_0(2\Delta(l-1)), \quad (12)$$

i.e., is bounded from both sides by monotonically decreasing functions of l .

(b) $\tilde{\sigma}_l^2$ decays as $1/\sqrt{l}$ when $l \rightarrow \infty$. In fact, bounds in Eq.(12) become very sharp for $l \gg 1$ and

$$\tilde{\sigma}_l^2 \rightarrow \Delta e^{-2\Delta l} I_0(2\Delta l) = \frac{1}{2} \left(\frac{\Delta}{\pi l} \right)^{1/2} + o\left(\frac{1}{\sqrt{l}}\right) \quad (13)$$

Inserting the latter expression into Eq.(10) and performing summation, we recover the result in Eq.(7).

Define now the following event: An N -step trajectory $X(t)$, Eq.(8), commencing at the origin, does not leave the interval $[-L, L]$, $L > 0$, or, in other words, that $\max|X(t)| \leq L$. Such an event takes place, clearly, when the absolute value of any ascending partial sum

$$X_k = \sum_{n=-\infty}^{\infty} \sum_{l=N-k+1}^N \sigma_l^{(n)} \zeta_{N-l}^{(n)}, \quad (14)$$

which define positions of the tagged monomer at consecutive discrete "time" moments k , $k = 1, 2, \dots, N$, is bounded from above by L .

However, in order to get a convenient "direction" of time in our final results, we will prefer to work with *descending* partial sums

$$Y_k = \sum_{n=-\infty}^{\infty} \sum_{l=1}^k \sigma_l^{(n)} \zeta_{N-l}^{(n)}. \quad (15)$$

Since, evidently,

$$Y_{N-k} + X_k \equiv X_N, \quad (16)$$

for any k , the trajectory $\{Y_k\}$ is exactly the trajectory $\{X_k\}$, with the only difference that it evolves in the inverse time $N - k$ and is shifted by a constant (realization-dependent) value X_N . Consequently, the survival probability $P_t = P(\max|X(t)| \leq L) = P(\max|Y(t)| \leq L)$.

To calculate $P(\max|Y(t)| \leq L)$, we proceed as follows. Let $I(\max|Y(t)| \leq L)$ be the following indicator function:

$$I(\max|Y(t)| \leq L) = \begin{cases} 1, & \max|Y(t)| \leq L, \\ 0, & \max|Y(t)| > L. \end{cases} \quad (17)$$

In terms of descending partial sums Eq.(17) can be rewritten as

$$I(\max|Y(t)| \leq L) = \prod_{k=1}^N I(|Y_k| \leq L). \quad (18)$$

Next, let $\text{rect}_L(x)$ be a rectangular function, such that:

$$\text{rect}_L(x) = \begin{cases} 1, & |x| < L, \\ 1/2, & x = \pm L, \\ 0, & |x| > L. \end{cases} \quad (19)$$

Representing $\text{rect}_L(x)$ via its Fourier transform:

$$\text{rect}_L(x) = \int_{-\infty}^{\infty} \frac{dy}{\pi} \frac{\sin(Ly)}{y} \exp[iyx], \quad (20)$$

we write down the indicator function in Eq.(18) as the following N -fold integral:

$$\begin{aligned} I(\max|Y(t)| \leq L) &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{k=1}^N \frac{dy_k}{\pi} \frac{\sin(Ly_k)}{y_k} \times \\ &\times \exp \left[i \sum_{k=1}^N y_k Y_k \right]. \end{aligned} \quad (21)$$

Now, in order to determine the desired probability P_t , we have to average the indicator function in Eq.(21) with respect to distributions of i.i.d. variables $\zeta_k^{(n)}$. To do this, we first rewrite the sum in the exponential in Eq.(21) in the following form

$$\sum_{k=1}^N y_k Y_k = \sum_{n=-\infty}^{\infty} \sum_{k=1}^N \zeta_{N-k}^{(n)} \left(\sigma_k^{(n)} \sum_{m=k}^N y_m \right). \quad (22)$$

Inserting the latter expression into Eq.(21) and performing averaging, we find that P_t is given by

$$\begin{aligned} P_t &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{k=1}^N \frac{dy_k}{\pi} \frac{\sin(Ly_k)}{y_k} \times \\ &\times \exp \left[-\frac{1}{2} \sum_{k=1}^N \tilde{\sigma}_k^2 \left(\sum_{m=k}^N y_m \right)^2 \right], \end{aligned} \quad (23)$$

where the effective variance $\tilde{\sigma}_k^2$ has been defined in Eq.(11).

Next, changing the integration variables:

$$\begin{aligned} Y_1 &= y_1 + y_2 + \dots + y_N, \\ Y_2 &= y_2 + y_3 + \dots + y_N, \\ Y_3 &= y_3 + y_4 + \dots + y_N, \\ &\dots \\ Y_N &= y_N, \end{aligned} \quad (24)$$

we obtain

$$\begin{aligned} P_t &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{k=1}^N \frac{dY_k}{\pi} \frac{\sin(L(Y_k - Y_{k+1}))}{Y_k - Y_{k+1}} \times \\ &\times \exp\left[-\frac{1}{2}\tilde{\sigma}_k^2 Y_k^2\right], \quad Y_{N+1} \equiv 0. \end{aligned} \quad (25)$$

Now, it is expedient to use the following integral identity for the sinc-function:

$$\frac{\sin(L(Y_k - Y_{k+1}))}{Y_k - Y_{k+1}} = \frac{1}{2} \int_{-L}^L dX_k \exp[iX_k(Y_k - Y_{k+1})]. \quad (26)$$

Plugging Eq.(26) into Eq.(25), and performing integrations over Y_k -s, we finally arrive at the following meaningful representation of the survival probability:

$$P_t = \int_{-L}^L \dots \int_{-L}^L \prod_{k=1}^N \frac{dX_k}{\sqrt{2\pi}\tilde{\sigma}_k} \exp\left[-\frac{(X_k - X_{k-1})^2}{2\tilde{\sigma}_k^2}\right], \quad (27)$$

where $X_0 \equiv 0$. The integrand in Eq.(27) represents the measure of trajectories of the zeroth monomer of an infinite discrete Rouse chain. Its continuous-space counterpart has been calculated previously in Ref. [3].

Heuristic estimate of P_t . – Changing the integration variables, $X_k = \tilde{\sigma}_k x_k$, we can cast Eq.(27) into the following form:

$$\begin{aligned} P_t &= \int_{-L/\tilde{\sigma}_1}^{L/\tilde{\sigma}_1} \int_{-L/\tilde{\sigma}_2}^{L/\tilde{\sigma}_2} \dots \int_{-L/\tilde{\sigma}_N}^{L/\tilde{\sigma}_N} \prod_{k=1}^N \frac{dx_k}{\sqrt{2\pi}} \times \\ &\times \exp\left[-\frac{1}{2}\left(x_k - \frac{\tilde{\sigma}_{k-1}}{\tilde{\sigma}_k} x_{k-1}\right)^2\right], \quad x_0 \equiv 0. \end{aligned} \quad (28)$$

Further on, since

$$\frac{\tilde{\sigma}_{k-1}}{\tilde{\sigma}_k} = 1 + O\left(\frac{1}{k}\right), \quad (29)$$

we may expect that, for sufficiently large k , this factor will not matter and

$$\left(x_k - \frac{\tilde{\sigma}_{k-1}}{\tilde{\sigma}_k} x_{k-1}\right)^2 \approx (x_k - x_{k-1})^2. \quad (30)$$

Hence, Eq.(28) can be approximated by

$$\begin{aligned} P_t &\approx \int_{-L/\tilde{\sigma}_1}^{L/\tilde{\sigma}_1} \int_{-L/\tilde{\sigma}_2}^{L/\tilde{\sigma}_2} \dots \int_{-L/\tilde{\sigma}_N}^{L/\tilde{\sigma}_N} \prod_{k=1}^N \frac{dx_k}{\sqrt{2\pi}} \times \\ &\times \exp\left[-\frac{1}{2}(x_k - x_{k-1})^2\right], \quad x_0 \equiv 0. \end{aligned} \quad (31)$$

One notices that the right-hand-side of Eq.(31) determines the probability that an N -step Brownian motion trajectory does not leave an interval whose boundaries move deterministically away from the origin as $\pm L/\tilde{\sigma}_k$, i.e., P_t can be approximately defined as

$$P_t \approx \int_{-L/\tilde{\sigma}_t}^{L/\tilde{\sigma}_t} P(X, t) dX, \quad (32)$$

where $\tilde{\sigma}_t \sim (\Delta^2/4\pi t)^{1/4}$, Eq.(13), while $P(X, t)$ obeys

$$\frac{\partial P(X, t)}{\partial t} = \frac{1}{2\Delta} \frac{\partial^2 P(X, t)}{\partial X^2}, \quad P(X, t=0) = \delta(X), \quad (33)$$

and

$$P(X = \pm L/\tilde{\sigma}_t, t) = 0. \quad (34)$$

We estimate next P_t defined by Eq.(32) using an adiabatic approximation discussed in Ref. [15]. The basic idea behind this approximation is that, if the boundary advances sufficiently slowly, the density distribution approaches the same form as in the *fixed* boundary case, except that the parameters in this probability distribution acquire time dependence to satisfy moving boundary conditions [15]. We find that, within this approximation, in the leading order

$$P(X, t) \approx \exp\left[-\frac{\pi^2}{8\Delta} \int_0^t \left(\frac{\tilde{\sigma}_\tau}{L}\right)^2 d\tau\right] \cos\left(\frac{\pi X \tilde{\sigma}_t}{2L}\right), \quad (35)$$

which yields the following estimate:

$$P_t \approx \exp\left[-\frac{\pi^2}{8L^2} \left(\frac{t}{\pi}\right)^{1/2}\right]. \quad (36)$$

Note that this estimate agrees with Eq.(1).

Rigorous bounds on the survival probability P_t .

– The N -fold integral in Eq.(27) can not be, of course, performed exactly and recourse has to be made to controllable approximations. Below we construct rigorous lower and upper bounds on P_t in Eq.(27), which both have the same time dependence defining in such a way an asymptotically exact (up to a constant factors in the characteristic relaxation time) result.

The method we use here is based on the approach outlined in Ref. [11] within the context of the Riemann-Liouville fractional Brownian motion. In constructing bounds, we will take advantage of the following two facts: (a) The effective dispersion $\tilde{\sigma}_k$ in Eq.(27) is a monotonically decreasing function of time.

(b) A fundamental property of P_t defined by Eq.(27) is that $P_t = P_t(\tilde{\sigma}_1, \tilde{\sigma}_2, \tilde{\sigma}_3, \dots, \tilde{\sigma}_N)$ is a monotonically decreasing function of any variable $\tilde{\sigma}_k$ [11].

This signifies that replacing any or all $\tilde{\sigma}_k$ by $\Sigma(k)$, such that $\tilde{\sigma}_k \leq \Sigma(k)$, we will decrease the survival probability and arrive at the *lower* bound on P_t ; if, on contrary, we will replace one or all $\tilde{\sigma}_k$ by $\tilde{\Sigma}(k)$, such that $\tilde{\sigma}_k \geq \tilde{\Sigma}(k)$, we

will *increase* the survival probability and obtain an *upper* bound on P_t .

We start with an upper bound on P_t . Since $\tilde{\sigma}_k$ is a monotonically decreasing function of k , we have that

$$\tilde{\sigma}_k \geq \tilde{\Sigma}(k) \equiv \tilde{\sigma}_N, \quad (37)$$

which holds for any k . The equality is attained only for $k = N$.

Hence, P_t in Eq.(27) is bounded from *above* by

$$\begin{aligned} P_t &\leq \int_{-L}^L \cdots \int_{-L}^L \prod_{k=1}^N \frac{dX_k}{\sqrt{2\pi}\tilde{\sigma}_N} \exp \left[-\frac{(X_k - X_{k-1})^2}{2\tilde{\sigma}_N^2} \right] = \\ &= \int_{-L/\tilde{\sigma}_N}^{L/\tilde{\sigma}_N} \cdots \int_{-L/\tilde{\sigma}_N}^{L/\tilde{\sigma}_N} \prod_{k=1}^N \frac{dx_k}{\sqrt{2\pi}} \exp \left[-\frac{(x_k - x_{k-1})^2}{2} \right] \end{aligned} \quad (38)$$

where $X_0 \equiv 0$ and $x_0 \equiv 0$.

Expression in the second line in Eq.(38) determines the probability that an N -step Brownian motion trajectory does not leave an interval with fixed boundaries $\pm L/\tilde{\sigma}_N$, which is a classic problem in the probability theory (see, e.g., Ref. [14]). Consequently, we find that at sufficiently large times

$$P_t \leq \exp \left[-\frac{\pi^2}{8} \frac{\tilde{\sigma}_N^2}{L^2} N \right] = \exp \left[-\frac{\pi^2}{16L^2} \left(\frac{t}{\pi} \right)^{1/2} \right]. \quad (39)$$

Consider now a lower bound on P_t in Eq.(27). To construct such a bound, we turn back to the definition of $\tilde{\sigma}_k$ in Eq.(11). Recollecting that $\exp(-x)I_0(x)$ is a monotonically decreasing function of x , we have that for any $u_1, u_2 \geq 0$,

$$e^{-u_1 - u_2} I_0(u_1 + u_2) \leq e^{-u_2} I_0(u_2). \quad (40)$$

Consequently, $\tilde{\sigma}_k^2$ is bounded as

$$\tilde{\sigma}_k^2 \leq \int_{\Delta(k-1)}^{\Delta k} du_2 e^{-u_2} I_0(u_2). \quad (41)$$

Further on, since for any $u_2 > 0$,

$$e^{-u_2} I_0(u_2) \leq \frac{1}{\sqrt{\pi u_2}}, \quad (42)$$

we have that the following bound holds:

$$\tilde{\sigma}_k^2 \leq \Sigma^2(k) = 2 \left(\frac{\Delta}{\pi} \right)^{1/2} (T_k - T_{k-1}), \quad (43)$$

where

$$T_k = k^{1/2}. \quad (44)$$

Hence, the survival probability P_t in Eq.(27) is bounded from *below* by

$$\begin{aligned} P_t &\geq \int_{-L}^L \cdots \int_{-L}^L \prod_{k=1}^N \frac{dX_k}{\sqrt{2\pi}\Sigma(k)} \exp \left[-\frac{(X_k - X_{k-1})^2}{2\Sigma^2(k)} \right] \\ &= \int_{-L(\frac{\pi}{4\Delta})^{1/4}}^{L(\frac{\pi}{4\Delta})^{1/4}} \cdots \int_{-L(\frac{\pi}{4\Delta})^{1/4}}^{L(\frac{\pi}{4\Delta})^{1/4}} \prod_{k=1}^N \frac{dx_k}{\sqrt{2\pi}(T_k - T_{k-1})} \\ &\times \exp \left[-\frac{(x_k - x_{k-1})^2}{2(T_k - T_{k-1})} \right], \quad X_0 \equiv 0, \quad x_0 \equiv 0. \end{aligned} \quad (45)$$

We notice now that the expression in the second line in Eq.(45) defines the probability that an N -step trajectory of Brownian motion, evolving in time T_t , Eq.(44), does not leave the interval $[-L(\frac{\pi}{4\Delta})^{1/4}, L(\frac{\pi}{4\Delta})^{1/4}]$. Hence, P_t in Eq.(27) is bounded from below by

$$P_t \geq \exp \left[-\frac{\pi^2}{8L^2} \left(\frac{4\Delta}{\pi} \right)^{1/2} T_N \right] = \exp \left[-\frac{\pi^2}{4L^2} \left(\frac{t}{\pi} \right)^{1/2} \right]. \quad (46)$$

This bound rules out an exponentially fast decay of the survival probability suggested in Ref. [9].

Finally, combining the lower and the upper bounds, we obtain the double-sided inequality obeyed by P_t , Eq.(3), which defines the decay of the survival probability P_t up to a numerical factor in the characteristic relaxation time.

Conclusions. – To conclude, we have studied the long-time asymptotical behavior of the probability P_t that a tagged monomer of an infinitely long Rouse chain will not escape, up to time t , from an interval $[-L, L]$. We have shown, by constructing rigorous lower and upper bounds on P_t , which both have the same dependence on time but slightly differ, by numerical factors, in the definition of the characteristic relaxation time, that P_t follows $\ln(P_t) \sim -t^{1/2}/L^2$. This decay law confirms our earlier predictions based on uncontrollable approaches [7, 8] and contradicts a recent prediction $\ln(P_t) \sim -t$ based on numerical simulations [9].

This result implies that the probability distribution function of the first-exit time from an interval $[-L, L]$ for the anomalous diffusion process executed by the tagged monomer of an infinitely long Rouse chain has a stretched-exponential tail $\sim \exp(-t^{1/2}/L^2)$ and thus has *all* moments.

We note that the obtained decay law agrees, as well, with the general result on the survival probability of the Riemann-Liouville fractional Brownian motion (fBm) in presence of absorbing boundaries [11] when the Hurst index $H = 1/4$. To realize that this is not a coincidence and the dynamics of a tagged monomer of an infinitely long Rouse chain is indeed in the fBm "universality class", consider Eq.(4), in which, for simplicity, we treat n as a continuous variable. Then, we have that $X_{n=0}(t)$ obeys

$$X_{n=0}(t) = \int_0^t \frac{\zeta_\tau d\tau}{(t-\tau)^{1/2}} \int_{-\infty}^{\infty} dn \exp \left[-\frac{n^2}{2(t-\tau)} \right] f_n, \quad (47)$$

where ζ_t is a white noise in time and f_n is a white noise of variable n , $-\infty < n < \infty$. Notice now that $\exp[-n^2/2(t-\tau)]$ is a bell-shaped function which broadens with time, which signifies that as time progresses, more and more monomers start to affect the dynamics of the zeroth monomer. Let us replace, for simplicity, $\exp[-n^2/2(t-\tau)]$ by a rectangular function $\text{rect}(n)$, such that $\text{rect}(n) = 1$ for $n \leq \sqrt{t-\tau}$ and $\text{rect}(n) \equiv 0$ for

$n > \sqrt{t - \tau}$. Then, Eq.(47) reads

$$X_{n=0}(t) \approx \int_0^t \frac{\zeta_\tau d\tau}{(t - \tau)^{1/2}} \int_{-\sqrt{t-\tau}}^{\sqrt{t-\tau}} dn f_n. \quad (48)$$

Now, one expects that, for typical realizations of f_n ,

$$\int_{-A}^A dn f_n \sim A^{1/2}, \quad (49)$$

and hence, $X_{n=0}(t)$ follows

$$X_{n=0}(t) \approx \int_0^t \frac{\zeta_\tau d\tau}{(t - \tau)^{1/4}}, \quad (50)$$

which is exactly the Riemann-Liouville fractional Brownian motion with Hurst index $H = 1/4$ studied in Ref. [11].

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